

**QUALITY
ASSURANCE
PLAN**

for

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President and Laboratory Director

Date

Laboratory Manager and QA/QC Officer

Date

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GENERAL QA/QC PROCEDURES

1. SAMPLES

1.1 Sampling Procedures It is the responsibility of the person collecting a sample to follow a sound sampling procedure. This will ensure that the sample collected is representative of the whole. Unless employees of Isotech do the sample collection, the entire responsibility for sample collection resides with the client. However, we at Isotech in addition to being available for sample collection, will provide advice on sampling methods, sample storage procedures, and sample size requirements.

1.2 Sample Containers Sample containers should be matched in size, type and condition to the anticipated analysis that will give best representation of the source, while preserving the sample integrity prior to analysis. Unless sample containers are provided by Isotech, the responsibility for adequate containers resides with the client. Again, in addition to being able to provide appropriate sample containers, shipping cartons and shipping instructions, Isotech will provide advice on sample containers/cartons and shipping procedures.

1.3 Sample Custody A completed "Chain of Custody" record is the responsibility of the client and, if required, should be submitted with the samples. Isotech will provide a "Chain of Custody/Request for Analysis" form if needed. Isotech assumes full responsibility for all samples received and stored for analysis at our laboratory. If any samples are removed from Isotech for additional analysis at other laboratories, a "Chain of Custody" form will be completed. All samples received for analysis are assigned a unique, non-duplicated laboratory number which is used as an identifier for each analysis performed.

2. INSTRUCTIONS AND PROCEDURES

2.1 Instrument Operation Procedures Analyses performed with manufactured analysis instruments are carried out by the methods either specified or recommended by the manufacturer of the instrument as identified in the instrument manual or provided by on-site training through the manufacturer's service technicians. Much of the operation of these instruments is controlled by personal computers utilizing software written and licensed by the manufacturers.

2.2 Analytical Procedures The analytical procedures used routinely at Isotech are described in written standard operating procedures (SOP's) for each analysis. Additional procedures may be used, as needed, in the process of satisfying a client's specific analysis requirements. These procedures will either follow published analytical methods, or methods developed at Isotech for a specific analysis. If the Isotech developed procedure becomes routine, then a standard operating procedure is written. All procedures are reviewed and approved by the laboratory supervisors. Various procedural tests and verifications performed are recorded in bound maintenance log books.

3. CALIBRATION AND STANDARDIZATION

3.1 Calibration Procedure and Frequency Depending on the analytical technique, instruments used for quantitative analyses are either calibrated at the beginning of every operating period or the calibration is checked by using a reference sample or a calibration standard. The instrument calibration is also checked at appropriate intervals during analyses. Specific instruments that form components of a sample preparation system are calibrated using duplicate sample analysis as well as analysis of a reference sample at appropriate intervals. Records of calibration results are kept in laboratory notebooks or other secure medium (see Documentation).

3.2 Method Validation Analytical methods are validated by one or more of the following techniques:

3.2.1 check or reference samples are analyzed and the results are compared with the internal documented or external certified (primary and secondary standards) values,

3.2.2 results from the candidate method are compared with those from another method known to be applicable and reliable, or

3.2.2 spiked samples and surrogate samples are analyzed and the method results are compared with the known concentrations.

3.3 Check/Reference Samples A check/reference sample is re-analyzed approximately every tenth analysis. This, in essence, results in a test of the method. Check/reference samples are chosen which have been analyzed many times over a period of years with consistent results.

3.4 Standards Primary standards are obtained from the International Atomic Energy Agency, Vienna, Austria, and certified by NIST (National Institute of Standards and Technology, formerly U.S. National Bureau of Standards) or directly from NIST. Secondary standards are obtained from commercially available sources recognized in the industry. Internal Reference standards are prepared by direct calibration against primary and secondary standards.

3.5 Duplicate Samples Duplicate analyses are performed approximately every tenth analysis. This duplicate sample analysis is performed approximately five analyses after the check/reference sample analysis is performed. Therefore, for a particular analysis procedure, a test of the method is performed every five analyses. This assures that at least 20% of all analyses are for maintaining QA/QC.

3.6 Specific Routine Procedures to Assess Performance Standard reference samples, chosen to match the submitted samples as closely as possible, in conjunction with duplicate samples and check samples, provide a matrix for performance evaluation. Control charts of replicate analytical data for reference samples are kept for each analytical method practiced routinely. Control charts are used to check the performance of an instrument and/or analytical technique.

Control charts for replicate samples are kept as tables and/or graphs. Graphs are displayed on the wall and data is plotted when measured to see if it falls within a predetermined acceptable range and to monitor for long term changes or trends. If a problem is detected with the reference sample, then the problem is first addressed by checking the integrity of the sample itself. Other reference samples are analyzed to determine if the problem persists. If reference sample integrity is verified, further diagnostic testing is carried out until the cause of the discrepancy is identified.

Isotech willingly participates in round-robin testing whenever the opportunity arises and recently participated in a hydrogen isotope study sponsored by the Finnigan Corporation. Cross-checks with the Illinois State Geological Survey are carried out frequently. Three natural gas standards set up by the International Atomic Energy Agency (IAEA) and now maintained by NIST are periodically analyzed. A supply of these standards is maintained and clients are encouraged to include one of these standards as a sample to be analyzed. Instrument calibration is carried out whenever analysis of internal standards and check samples suggests a potential problem.

3.7 External Quality Control Checks Blind duplicates, check samples, blanks, and spiked samples may be submitted by the client, and this practice is encouraged.

4. ANALYSES AND ANALYTICAL RESULTS

4.1 Data Reduction and Reporting Calculations made in reducing raw data to reportable form are verified (preferably by a second person) before reporting the results to the client. If a computer program is used to perform calculations, the accuracy of the input data is verified by comparison with the raw data. In all cases where computer programs are used to make the calculations, the person making the calculations verifies that the proper program is used. Data reduction and calculation is performed automatically by the computers which control the instruments. Reported results are verified relative to the computer printouts. This verification involves copying the value from the printout to a report format and is generally performed by the same person who performed the analyses.

4.2 Hard Copy and Electronic Data Deliverables Normally, final data is emailed to clients as an Excel workbook file, and also a PDF version of the data. Depending on the sample type, hard copy reports can be either a single page per sample, or can be in tabular format with multiple samples per page. Hard copy reports are mailed to clients, unless clients indicate that the email versions are sufficient for their needs. Upon request, CD's will be submitted to clients in addition to the hard copy reports. Also, appropriate graphs will be provided upon request. Compositional analyses for natural gas samples are normalized to 100% when the Analysis Report is generated. Upon request a QA/QC report containing results for all check samples and duplicates as well as copies of raw data can be provided at additional cost.

4.3 Documentation All laboratory notes, observations, calibrations, manual calculations, and any other pertinent information are kept in bound laboratory notebooks or other secure recording medium. Computer programs used for data storage, retrieval, and calculations, which are developed within Isotech Laboratories, Inc., are documented well enough that someone not intimately familiar with the program development, but who is familiar with the programming language, can understand the operation of the program. Printed and dated copies of the current version and each previous version (insofar as possible) of the program are kept in the developer's files. These copies remain at and are the property of Isotech, should the developer leave employment of Isotech Laboratories, Inc. Electronic backup copies of currently-used computer programs are securely kept by the program's developer or principal user. Computer software provided by the instrument manufacturers that reduces raw data and calculates results have been checked by doing the calculations manually. Backup copies of analyses databases are made periodically. The frequency of making backup copies depends on the frequency of updating the database, but the minimum frequency for making backup copies is weekly. All laboratory notebooks, data, computer programs, computerized databases, and any other means of recording data, observations, calculations, and other pertinent information developed at or on behalf of Isotech, remain the property of Isotech Laboratories, Inc., unless otherwise designated by the Board of Directors of Isotech Laboratories, Inc.

4.4 Hard Copy Data Files and Storage All pertinent paperwork associated with each batch of samples is stored in the client files. Typical paperwork can include chain of custody records, client analysis requests, email communication to/from clients regarding samples, final data, and cover letter mailed to client with final data. Data files are kept indefinitely unless clients request that we dispose of them.

5. MAINTENANCE AND REPAIR

5.1 Instruments Each instrument or machine used to produce quantitative analysis results, or leading up to their production, undergoes periodic preventive maintenance according to manufacturer's instructions, or some established preventive maintenance schedule. Preventive maintenance may be done by laboratory personnel, manufacturer's representative, or a qualified third-party contractor, depending on the abilities of the laboratory operator and the complexity of the equipment. Records of repairs and preventive maintenance are kept by the appropriate laboratory personnel in files or notebooks. Records of equipment problems and solutions are kept in files or notebooks. The analyst is the person best qualified to recognize when the instrument or machine they operate is in need of repair, or the method they practice is in need of corrective action. They are aided in this monitoring by control charts. Corrective action is needed when predetermined limits for data acceptability are exceeded. Analysts are also to use their experience and scientific judgment in deciding when corrective action is needed.

5.2 Other Equipment Other laboratory equipment such as vacuum pumps, ovens, test meters and non-instruments such as glassware are maintained by Isotech personnel. In most cases this is performed by the same person who utilizes the equipment for analysis. Visual checks backed

by mechanical and electronic gauges provide constant maintenance checks directly to the operators.

6. REVIEW

6.1 Analytical Review At the time of each analysis or sample preparation, the staff chemist performing the analysis reports anomalies to the Laboratory Manager, who is the primary QA/QC officer. Staff chemists are all trained on a variety of techniques and work closely together. Constant communication between staff members results in most problems being addressed when they occur. Unusual problems are brought to the attention of the Laboratory Director. Whenever possible, a sample that is questionable for any reason is re-analyzed to verify results, regardless of when the sample was analyzed initially. This means that more than 10% of samples will be duplicates if the data appears to be unusual in any way.

Before final reports are printed, data is checked to verify that the final data agrees with the raw printouts, and raw percentages for compositional analyses are checked to ensure that all components are identified. Reproducibility of duplicate isotopic samples is compared to stated precision limits. Analytical data is reviewed for anomalies by both the QA/QC Officer and the Laboratory Director prior to reporting.

6.2 Standard Operating Procedures (SOP's): These procedures are developed from specific analytical methods for operating specified equipment and supplies to obtain high quality data reflective of each sample analyzed. In addition to revisions due to procedural or equipment changes these SOP's are reviewed by the Laboratory Manager annually.

7. QA/QC PROBLEM REPORTING

7.1 Responsibilities QA/QC is the responsibility of every person who collects or analyzes samples. If any Isotech Laboratories, Inc. employee observes any QA/QC problem, that employee will discuss the problem with the analyst, QA/QC officer, or Isotech Laboratories, Inc. Board Member. No negative action will be ever be brought against nor will accrue to any staff member who reports QA/QC problems.

8. SUBCONTRACT POLICY

Samples for analysis of ^{14}C (radiocarbon) are converted to purified carbon dioxide and then submitted to an established radiocarbon dating laboratory for the final analysis. When analyses are requested for which Isotech does not have either the necessary equipment or expertise to provide high quality results, these analyses too may, with the knowledge of the client, be submitted to a subcontract laboratory. Only established, reputable laboratories which maintain strict QA/QC control are utilized. All samples are prepared and packaged using techniques that have been recommended or approved by the subcontract laboratory. Analysis of reference

samples and standards is the responsibility of the subcontract laboratory. Duplicate analyses of samples submitted to a subcontract laboratory should be requested by the client and will be charged as regular samples.

APPENDICES: ANALYTICAL PROCEDURES

I. Sample Preparation Procedures for Stable Isotope Analyses

A. Procedures for Stable Isotope Analysis of Water Samples

1. $\delta^{13}\text{C}$ (Carbon Isotope Analysis) of Dissolved Inorganic Carbon (DIC)

Equipment and Supplies

Vacuum pumps and gauges
Glass and metal vacuum system
Dry ice
Isopropyl alcohol
Liquid nitrogen
Phosphoric acid
Gas-Oxygen torch

Method/Procedure The $\delta^{13}\text{C}$ of DIC is determined by injecting up to 20 ml of sample water into an evacuated 60 ml serum bottle containing 2 ml of 85% phosphoric acid and a magnetic spin bar. Sample size is determined based on alkalinity, which is measured by titration with 0.1N HCl.

The sample is stirred for a minimum of 15 minutes and then connected to the vacuum system via a needle port. The hypodermic needle is embedded into the stopper and the air within the needle port is evacuated. The needle is then inserted completely through the stopper. The CO_2 generated is liberated from the water and transferred through a trap cooled in a dry-ice/isopropyl-alcohol mixture (for H_2O removal) to a U-trap which is cooled in liquid nitrogen. The sample is constantly stirred to ensure that all CO_2 is liberated from the water. All residual gases are pumped away through the vacuum system. The CO_2 is transferred into a Pyrex cold finger for yield determination by placing a Dewar of dry ice slush on the U-trap to liberate the CO_2 and placing a Dewar of liquid nitrogen on the cold finger to collect the CO_2 . The sample is sealed into the cold finger and the liquid nitrogen Dewar is removed to allow the sample to sublime. The yield is calculated from the pressure reading on a digital manometer connected to the cold finger.

The CO_2 is then collected in $\frac{1}{4}$ " OD Pyrex tubing by transferring the purified CO_2 into the seal tube with liquid nitrogen. The tube is fused shut with a gas-oxygen torch and tagged with a piece of label tape for mass spectrometric analysis.

Maintenance The system is thoroughly evacuated between samples. Vials are washed and dried.

Replication At a minimum, every tenth analysis is a replicate.

Calculation Calculations are performed by the software on the IRMS (Isotope Ratio Mass Spectrometer) at the time of final analysis.

Documentation All procedural tests and verifications performed are recorded in bound maintenance log books. All sample data including the date prepared with analyst identification are recorded on laboratory log sheets and in bound log books.

2. δD (Hydrogen Isotope Analysis) and $\delta^{18}\text{O}$ (Oxygen Isotope Analysis) of H_2O

Equipment

3mL syringes

0.2 micron syringe filters

2mL glass vials with septum caps

Picarro CRDS (cavity ringdown spectrometer) model L1102-i fitted with a Leap autosampler

Method/Procedure

Water samples are individually filtered into 2mL vials with 0.2 micron syringe filters. If samples are high salinity brines, they should be vacuum distilled prior to loading. The vials are then loaded onto trays which are installed on the autosampler. Samples are analyzed by the CRDS in replicate in accordance with the manufacturer's recommendation.

Reference Sample Two reference water samples are used to verify accuracy and reproducibility. These reference waters are analyzed approximately every tenth analysis. Performance is also periodically checked by direct analysis of primary reference standards obtained from IAEA or NIST.

Replication

At a minimum, every tenth sample analysis is a replicate.

Calculation

Calculations are performed by the software on the CRDS at the time of analysis.

Documentation

All procedural tests, sample preparations and verifications performed are recorded in bound maintenance log books. All final data including the date prepared with analyst identification in bound log books.

3. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (Nitrates)

Equipment and Supplies

Filter paper
Glass filtration apparatus
1N HCl
BaCl₂
Borosilicate glass balls
Hot Plate
Cation exchange resin
Anion exchange resin
1N HBr
Ag₂O
DI Water
Flasks
Stirbars
Glass funnel
Freezer
Oven
Freeze-dryer
Teflon beakers

Method/Procedure Nitrate is extracted from groundwater samples and converted into AgNO₃ using ion-exchange techniques. Samples are filtered and pH adjusted to 1-3 using 1N HCl boiled to final volume of 250 ml. BaCl₂ is added to remove dissolved sulfates. The sample is poured into separatory funnels and passed through a pretreated cation exchange column. The sample is then passed through the anion column, where nitrate is held within the column. 1N HBr is added, and the eluate collected, diluted with 20mL DI water, and Ag₂O is added. The sample is filtered, frozen in a Teflon beaker, and placed in a freeze drying vacuum oven until only the AgNO₃ crystals remain. The crystals are then analyzed using $\delta^{15}\text{N}$ using an EA and isotope ratio mass spectrometer (IRMS) and the $\delta^{18}\text{O}$ values measured using a TCEA-IRMS.

B. Procedures for Stable Isotope Analysis of Gas Samples

1. $\delta^{13}\text{C}$ and δD (Carbon and Hydrogen Isotope Analysis) for Hydrocarbon Gases, Offline Prep Systems

Equipment and Supplies

3 SRI 8610C Gas chromatographs
Evacuated transfer system
Copper oxide combustion furnace

Dry ice
Isopropyl alcohol
Liquid nitrogen
Electronic manometer
Electronic vacuum gauge
Helium
Oxygen
Gas-oxygen torch

Method/Procedure The determination of carbon and hydrogen isotopic ratios for hydrocarbons in gas mixtures (e.g. natural gas) requires a sample preparation system capable of first separating the individual hydrocarbons and then quantitatively converting them into carbon dioxide (CO₂) and water for mass-spectrometric analysis. There are 2 systems utilized for processing natural gases. The systems employed are helium purged flow systems consisting of two major units.

The first unit consists of sample injection syringes, SRI 8610C gas chromatographs, a personal computer, and several flow-control valves. This configuration separates the hydrocarbon of interest from the sample and channels it into the combustion-collection unit. The second unit is the combined combustion-collection unit which includes quartz combustion tubes filled with cupric oxide (CuO), and vacuum lines. This system converts the hydrocarbon of interest into CO₂ and water, which are then collected and purified for isotopic analysis.

Samples can be analyzed from a variety of different sampling containers such as high-pressure cylinders, gas bags, or vacutainers. The sample is expanded into the injection syringes which have been pre-set to the desired volume, and adjusted to atmospheric pressure. Once the sample is loaded into the injection syringe, the separation is automated by both a personal computer and on-board computers within the gas chromatographs. Once a run is initiated, the GC software controls valves to the injection syringes, and controls the valves to the separation columns.

The sample hydrocarbon is flowed through a copper oxide combustion furnace set at 850°C utilizing helium as the carrier gas. On the downstream side of the furnace, both the carbon dioxide and the water of combustion are collected in a liquid nitrogen-cooled trap. Once the entire sample has been collected, the helium carrier gas is evacuated. The carbon dioxide is then transferred into a cold finger attached to a digital manometer for yield measurement by placing a dewar of dry ice slush on the collection trap to liberate the CO₂ while maintaining the water in the collection trap. Once all of the CO₂ has been collected in a cold finger, the valve to the cold finger is closed and the liquid nitrogen is removed to allow the CO₂ to sublime for yield determination.

The water of combustion is then transferred into a 12-inch length of ¼" OD Pyrex tubing that has been sealed at one end and contains a weighed quantity of zinc turnings. The zinc is prepared by evacuating and heating to 400°C for at least 5 minutes while open to vacuum. Once the sample water has been completely transferred into the sample tube and frozen with liquid nitrogen, the sample tube is sealed off with a torch for later mass spectrometric analysis.

After the water has been sealed off, the pressure reading on an electronic pressure gauge connected to the coldfinger is used to calculate the yield of CO₂, and this is recorded in the lab notebook. The CO₂ is then transferred into ¼” OD Pyrex tubing and sealed with a torch for later mass spectrometric analysis.

Maintenance The packed columns used for GC separation are backflushed after every sample and serviced when the peak separation decreases. This service consists of baking at manufacturer's recommended temperature and time. During the heating and cooling process, O₂ is flowed through the copper oxide combustion furnaces to regenerate the CuO. This conditioning process is completed each day samples are analyzed. The transfer/collection system is thoroughly evacuated between samples. Valve o-ring seals within the evacuated transfer system are replaced as required.

Reference Samples The system is tested by analyzing a reference sample every tenth analysis performed.

Replication A duplicate analysis of one of the samples is performed approximately every tenth analysis. This duplicate analysis is performed approximately five analyses after the reference sample analysis is performed. Therefore, a test of the system operation is performed every five analyses.

Calculation The expected yield is calculated from the injection volume and the hydrocarbon concentration

Documentation All procedural tests, sample preparations and verifications performed are recorded in bound maintenance log books. All final data including the date prepared with analyst identification are recorded on laboratory log sheets and/or in bound log books. Digital copies of all chromatograms are stored and backed up regularly.

2. $\delta^{13}\text{C}$ (Carbon Isotope Analysis) of CO₂, Offline Prep Method

Method/Procedure Preparation of samples for measurement of the $\delta^{13}\text{C}$ of CO₂ is performed on the same system as the hydrocarbons. The procedure is identical to that for the hydrocarbons, with two exceptions. First, CO₂ does not pass through a combustion furnace; gas is channeled directly from the GC outlet to the collection trap. Second, there is no water of combustion. Therefore, the collection/purification system is slightly smaller as it has only one sample tube, and all steps related to collecting the water of combustion are omitted.

3. GC-C-IRMS systems, $\delta^{13}\text{C}$, δD , and $\delta^{15}\text{N}$

Equipment and Supplies

HP6890 GC interfaced to ThermoFinnigan Delta Plus Advantage
HP6890 interfaced to Thermo Electron Delta V Plus
HP 6890 interfaced to Thermo Scientific Delta V Plus

CTC Analytical GC PAL autosampler

Method/Procedure

GC-C-IRMS systems, also referred to as “online” or “continuous flow”, consist of an Agilent 6890 GC combustion unit and Finnegan GCCIII interfaced with a mass spectrometer (Delta V Plus or Delta Plus Advantage), and are used to analyze the carbon isotopic value of hydrocarbon components in gas samples. Samples are injected into the HP6890 split/splitless injector either manually, or using customized GC PAL auto-samplers. The hydrocarbon components are separated by the GC column in the HP6890, and each individual component slated for isotopic analysis is combusted in a combustion furnace supplied by the instrument manufacturer. The resultant CO₂ is introduced directly into the mass spectrometer, and Finnegan’s Isodat software is utilized for peak detection and quantification.

Hydrogen isotopic values for methane are completed using the same system, but the gas is channeled through a high-temperature pyrolysis furnace instead of through the combustion furnace. The pyrolysis furnace converts methane into H₂ and carbon, and the H₂ gas is introduced directly into the mass spectrometer.

Nitrogen isotopic data for elemental nitrogen (N₂) is generated using the same system, with one key difference: the temperature on the combustion reactor is reduced so that the N₂ is not oxidized.

Maintenance

Septa on the GC inlet system are replaced daily when the system is operational. Pyrolysis and combustion tubes are replaced as needed. Combustion tubes are oxidized daily during analysis sequences.

Reference Samples

Reference gases are analyzed at the start of each analysis sequence, and then at least 10% of all analyses during a sequence are check samples.

Replication

At least 10% of client samples are analyzed in duplicate.

C. Procedures for Stable Isotope Analysis of Organic Solids and Liquids

Equipment and Supplies

Carlo Erba Elemental Analyzer connected to a Finnigan Delta S Mass Spectrometer
ThermoElectron TCEA interfaced to a Thermo Electron Delta V Plus Mass Spectrometer

Elementar EL Vario III interfaced to a Thermo Scientific Delta V Plus Mass Spectrometer

Method/Procedure The determination of carbon, nitrogen, oxygen, hydrogen, and sulfur isotopic ratios for organic solids and liquids is accomplished by combustion or pyrolysis of the materials for mass-spectrometric analysis. The systems employed are standard elemental analyzers with carousel auto samplers, connected to isotope ratio mass spectrometers through an interface supplied by the manufacturer. The combustion products of interest from the elemental analyzers are: carbon dioxide (CO₂) for carbon isotope analysis, N₂ for nitrogen isotope analysis, and sulfur dioxide (SO₂) for sulfur isotope analysis. Oxygen and hydrogen isotopic ratios are analyzed on the TCEA, which converts hydrogen from the organic materials to H₂ gas for hydrogen isotopic measurements, and oxygen within the organic materials is converted to carbon monoxide (CO) for oxygen isotope analysis. This system in its entirety was purchased expressly for analysis of these samples.

Samples are weighed on a Mettler balance and loaded into a standard EA tin capsule for carbon, nitrogen, or sulfur isotopic analysis, or into a silver capsule for oxygen or hydrogen isotopic analysis. Once the samples are loaded into the EA, a run is started and all instrument control is done by software provided by the MS manufacturer. Samples are combusted as per normal EA operating procedures, and the CO₂, N₂, and SO₂ are separated by the EA. Similarly, the pyrolysis products H₂ and CO from the TCEA are separated within the instrument. The vents of the EA and the TCEA are connected to the mass spectrometers via the interface, where a small portion of the EA or TCEA output flows directly into the MS. The MS measures the isotopic value of the component of interest (CO₂, N₂, SO₂, CO, or H₂) and the final isotopic value is generated by software provided by the manufacturer.

Maintenance Ash is removed from the top of the combustion column in the EA or the top of the pyrolysis reactor in the TCEA as directed by the manufacturer, or when peak tailing becomes apparent. Combustion and reduction furnaces in the EA are replaced at appropriate intervals as outlined by the dealer, or when peak shape deteriorates. The TCEA contains glassy carbon, which is periodically replaced.

Reference Samples The systems are tested by analyzing at least one reference at least once per batch of 25 samples loaded into the auto sampler. A blank is also run at the start of each batch.

Replication Approximately 10% of all samples analyzed are replicates.

Documentation All final data including the date analyzed are recorded on laboratory log sheets and/or in bound log books. Digital copies of chromatograms are stored and backed up regularly.

II. Sample Preparation Procedures for Radiogenic Isotope Analyses

A. Procedures for Radiogenic Isotope Analysis of Gases

1. ^{14}C (Radiocarbon) and ^3H (Tritium) in CH_4 (Methane) by Radiometric Analysis

Equipment

Peristaltic pump
Flow meters
Gas regulators
Vacuum gauge
Molecular sieve trap
High temperature tube furnaces
Quartz combustion chamber
Vacuum traps and gauges
Vacuum pumps
Mercury manometer

Method/Procedure

1.1 Methane Combustion

The system used for tritium (^3H) analysis of methane and for radiocarbon (^{14}C) analysis of methane consists of a peristaltic pump, a CO_2 removal unit, and a sample combustion/collection flow unit. The CO_2 removal unit includes a trap filled with molecular sieve and an ascarite backup trap. The combustion/collection unit is composed of a tube furnace, an inner and an outer quartz combustion tube which are interconnected through an orifice located at the tip of inner tube, a flow control valve, and a series of gas purification and collection traps. The system is attached to a vacuum manifold.

The molecular sieve is baked and evacuated to 350°C before each use to ensure that all absorbed gases are removed from the trap. After the molecular sieve is cooled to room temperature, the system is first evacuated, and then pressurized with argon. Oxygen is then introduced into the outer combustion tube which is partly filled with cupric oxide (CuO) and placed in a tube furnace preheated to 850°C . After the flow is established, the gas sample enters the system through a flow control valve (if the sample is above atmospheric pressure) or is pumped in slowly by a peristaltic pump (if the sample is at or below atmospheric pressure). CO_2 associated with the sample is absorbed by the molecular sieve and removed from the sample quantitatively. Methane in the sample is then carried by argon through the inner combustion tube and ignited at the tip of the tube where oxygen is supplied.

The water of combustion is collected in a trap immediately after the combustion furnace. This collection trap is heated under vacuum prior to each analysis to ensure that there is no cross-contamination between samples. To collect the sample water, the trap is immersed in a dry ice/isopropanol bath. Once the entire sample has been combusted, the frozen water of combustion is melted and transferred to a glass vial to await tritium analysis.

The CO₂ formed by combustion is collected in two liquid nitrogen cooled traps, measured volumetrically, and transferred into a storage cylinder. Storage cylinders are effectively leak-tested during each use by evacuation prior to transferring the sample CO₂. Each cylinder is tagged with sample identification and is forwarded to a subcontractor for ¹⁴C analysis along with a chain-of-custody form.

If the yield of CO₂ is less than one liter, the sample is diluted to approximately one liter with ¹⁴C free CO₂ prepared from the combustion of natural gas. The dilution gas has been analyzed to verify that it is ¹⁴C free, and found to be statistically indistinguishable from background. The volume of the sample and the volume of the dilution gas are precisely measured with a mercury manometer. The dilution factor measured is used in the final calculation of the ¹⁴C activity.

1.2 Tritium Analysis

The water of combustion from methane samples is ready to be analyzed in the liquid scintillation (LS) spectrometer. There is no pre-treatment necessary for the sample, as it is essentially distilled water when it is collected.

The scintillation counting vials are prepared by pipetting 10 ml of commercial scintillation cocktail into a 20 ml plastic vial and then weighing to ±1 mg. The sample is then pipetted or poured into the counting vial and the vial is re-weighed. If the amount of sample is less than 10ml, then tritium-free water is added to bring the total volume of water to about 10ml. Details of the tritium analysis procedure are given later in this document.

Maintenance After each sample, the molecular sieve is baked and evacuated at 350°C. The vacuum system is thoroughly evacuated to remove all residual gas and water vapor after each sample. The water trapping system is disassembled and thoroughly dried and evacuated after each sample.

Calibration/Standardization Gas storage volumes have been calibrated using known quantities of carbon dioxide gas. No further standardization of this system is necessary. Calibration and standardization of the final ¹⁴C analysis is performed by the subcontracted laboratory.

Replication and Reference Samples Replicate or reference sample analysis for these analyses are performed only when requested and supported by the client.

Calculation Yields are calculated by comparing the volume of CO₂ generated and the weight of the water collected to the amount expected based on the amount of CO₂ collected. ¹⁴C concentrations are determined by the subcontracted laboratory and corrected for isotope fractionation by Isotech's database program.

2. ¹⁴C (Radiocarbon) in CO₂ by Radiometric Analysis

Equipment

Same as for ^{14}C of CH_4

Method/Procedure After the CO_2 from methane has been collected as described in the previous section, the expansion cylinder and the collection traps are evacuated. The argon carrier gas trapped in the molecular sieve is evacuated and then a tube heater is placed on the molecular sieve trap. The trap is heated to 350°C to liberate the sample CO_2 from the molecular sieve. The CO_2 is then transferred via a shunt to the CO_2 collection system. The CO_2 is collected in a liquid nitrogen-cooled trap. Once the sample has been transferred into the collection traps, the sample yield is measured and the sample is transferred into a storage cylinder using the same method as for methane. The purified CO_2 is then submitted to a subcontract laboratory for radiometric analysis of ^{14}C .

3. ^{14}C (Radiocarbon) in CH_4 and CO_2 by Accelerator Mass Spectrometry (AMS)

Equipment:

Same as for $\delta^{13}\text{C}$ of CO_2 and $\delta^{13}\text{C}$ of Hydrocarbons.

Method/Procedure:

The same method is employed for sample preparation as for $\delta^{13}\text{C}$ of either CH_4 or CO_2 . Once the purified CO_2 has been sealed into Pyrex tubing, the tube is tagged with a piece of label tape and sent to the subcontractor along with a chain of custody form for ^{14}C analysis. When there is only enough material available for one sample preparation, the $\delta^{13}\text{C}$ is first determined by MS analysis. Then the sample is frozen back out of the MS with liquid nitrogen and sealed into the same Pyrex tubing before shipment to the subcontractor. A longer sample tube is used on the initial sample preparation to ensure that there is sufficient tube available for sealing after MS analysis. The sealed sample is then submitted to a subcontract laboratory for ^{14}C determination by accelerator mass spectrometry.

B. Procedures for Radiogenic Isotope Analysis of Water

1. ^{14}C (Radiocarbon) in dissolved inorganic carbon (DIC) by Accelerator Mass Spectrometry (AMS)

Equipment

Same as for $\delta^{13}\text{C}$ of DIC.

Method/Procedure

The same method is used as for $\delta^{13}\text{C}$ of DIC. Once the purified CO_2 has been sealed into Pyrex tubing, the tube is tagged with a piece of label tape and sent to the subcontractor, along with a chain of custody form, for ^{14}C analysis. When there is only enough material available for one sample preparation, the $\delta^{13}\text{C}$ is first determined by MS analysis. Then the sample is frozen back out of the MS with liquid nitrogen and sealed into the same Pyrex tubing before shipment to the subcontractor. A longer sample tube is used on the initial sample preparation to ensure that there is sufficient tube available for sealing after MS analysis. The sealed sample is then submitted to a subcontract laboratory for ^{14}C determination by accelerator mass spectrometry.

2. ^3H (Tritium) in H_2O

Equipment

Vacuum pumps and gauges
Distillation column
Electrolytic enrichment cells
Electrolysis power source and cooling system
Liquid scintillation counting system
Assorted chemicals and glassware
Dry ice/ isopropyl alcohol
Drying oven

Method/Procedure--Direct Counting of Higher Tritium Content Water (greater than 15 TU).

Approximately 15ml of the water sample is treated with 0.1 M KMnO_4 at 70°C for about an hour. This sample is then vacuum distilled. Ten ml of the distillate is accurately weighed and mixed with 10ml of an appropriate organic scintillator cocktail in a 20ml plastic vial and counted in a liquid scintillation spectrometer for 1000 minutes. Background and a NIST standard are also similarly counted and the tritium content calculated.

Method/Procedure--Enrichment of Lower Tritium Content Water (less than 15 TU).

About 300 ml of the water sample is conventionally distilled to near completion. Exactly 200g is added to an enrichment cell along with 2ml of 9M tritium-free sodium hydroxide and is electrolytically enriched down to about 11-13 ml (final weight is exactly determined), and then neutralized with carbon dioxide for 20 minutes. The enrichment procedure is carried

out under conditions of about 2°C and constant voltage of 4V. Ten ml of the enriched sample is accurately weighed and mixed with an appropriate organic scintillator cocktail in a 20 ml plastic vial and counted in a liquid scintillation spectrometer for 1000 minutes. Background and a NIST standard are also similarly counted and the tritium content calculated.

General QA/QC Procedures include critically reviewing TU/cpm/g of NIST standard versus existing data, critically reviewing background cpm versus existing data, and comparing data from splits of NIST and other samples with outside established laboratories. A criteria of exceeding 1 sigma limits from existing data triggers investigation of possible errors. Electrolytic enrichment cells are calibrated using working standards approximately every 6 months, or whenever duplicates prepared in different cells suggest a possible change in enrichment factor.

Maintenance The vacuum system is thoroughly evacuated between samples. All glassware and electrolytic cells are cleaned with deionized water and baked out at about 130° C between samples.

Replication At a minimum, every tenth analysis is a replicate. Periodically a blind split is sent to another established tritium analysis laboratory for check purposes.

Reference Sample A NIST water standard (a dilution of NIST 4361B) is used for each sample set to verify accuracy and reproducibility. A glass-sealed high tritium sample is routinely checked to verify that the counter is operating satisfactorily. QA/QC plots are maintained for both standard and background counts using deviation of 1 sigma as a criteria for a more detailed evaluation of the data.

Calculation Calculations are performed utilizing a spreadsheet to calculate tritium concentration in TU on the date counted.

Documentation All procedural tests, sample preparations and verifications performed are recorded in bound maintenance log books. All final data including the date prepared, with analyst identification, are recorded on laboratory log sheets or in bound log books.

III. Dual Inlet Mass Spectrometric Analysis

A. Measurement of $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ in CO_2

Equipment Finnigan MAT Delta S Isotope Ratio Mass Spectrometer

Method/Procedure Because $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ analyses are performed simultaneously, the procedure described here generates both measurements. A mass spectrometric analysis involves comparisons of a sample to a reference standard; in this case the comparisons are measurements of mass 44, 45, and 46, giving the both the oxygen and carbon isotopic compositions. This is accomplished by a dual inlet system where the sample and the reference standard are measured alternately. At the beginning of each day, a reference standard is introduced into the standard side of the inlet system, and this gas is generally used for the entire session. There are two different reference standards in aluminum cylinders which are permanently mounted on the MS inlet system. The sample to be analyzed against the standard is introduced into the system via an evacuated inlet system and tube-cracker. With the inlet system fully evacuated, the sample (which is sealed into $\frac{1}{4}$ " Pyrex tubing) is introduced by breaking the glass sample tube and allowing the sample to fill a variable volume bellows. Once the sample has been introduced into the MS, the actual analysis is computer controlled using equipment obtained from the manufacturer. Each analysis is given a specific reference name and/or number, utilizing the lab number as the primary reference. Final results are calculated by the manufacturer's software, and are stored on the hard drive of the computer, recorded in a bound lab notebook, and stored as the computer generated printout.

Maintenance The source region of the MS is periodically disassembled and cleaned. The filament is replaced as needed. Oil levels in mechanical vacuum pumps are checked frequently and maintained at the proper level. Turbomolecular pumps are lubricated according to the manufacturer's recommendations.

Calibration/Standardization The first analysis of each session is a zero enrichment, where the working standard is analyzed against itself to check machine stability. Isotope ratio determination involves multiple direct comparisons of the sample to a reference standard (generally at least 6 comparisons). Stable carbon and oxygen isotope compositions are always reported as the difference between the ratios of the two isotopes of interest in the sample and the ratio in a primary reference standard. That is,

$$\delta X_{(\text{sample})} = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \times 1000$$

Where X represents the isotope of interest, ^{13}C or ^{18}O , and R represents the ratio of $^{13}\text{C}/^{12}\text{C}$, or $^{18}\text{O}/^{16}\text{O}$. The δ value is expressed in terms of per mil (‰), or parts per thousand.

In practice, the difference between the sample and an internal reference standard is measured and then the value relative to the primary standard is calculated by the instrument manufacturer's software. Two internal reference standards are used at Isotech, both of which have been calibrated multiple times over the past 20 years relative to several standards (graphite, oil, carbonates, waters, etc.) available from the International Atomic Energy Agency and the National Institute of Standards and Technology, in at least two different laboratories and on up to five different mass spectrometers. Standardization of the mass spectrometer involves analyzing one the reference standards against the other (the reference standard used for the actual analysis is chosen according to the types of samples to be analyzed). This standardization is carried out at least once each day that analyses are to be conducted. In the rare event that the value obtained differs by more than 2 standard deviations from the expected value, the standardization is repeated with new aliquots of the reference standards. If the difference persists, the calibration of the reference gases is checked by having them analyzed by another laboratory, or by recalibrating them relative to NIST or IAEA standards.

Replication Because of replicate sample preparations, at least 10% of all analyses are replicates.

Reference Samples Because 10% of all samples prepared for stable isotope analysis are check samples or reference samples which have been previously analyzed, these samples also serve as check samples for the mass spectrometer.

Calculation All calculations are performed by the software obtained from the manufacturer.

B. Measurement of $^2\text{H}/^1\text{H}$ (Deuterium/Hydrogen) in H_2

Equipment

Finnigan Delta Plus XL isotope ratio mass spectrometer
Aluminum heating block
Personal computer

Method/Procedure The H_3 factor, which is the portion of the mass 3 signal attributable to $^1\text{H}-^1\text{H}-^1\text{H}$ (instead of $^2\text{H}-^2\text{H}$), is determined before each run early in the day and periodically throughout the day based on machine performance (if the values start drifting, a new H_3 factor is determined). The reference standard must be replenished at least once during an 8 hour period.

Water samples for deuterium/hydrogen analysis are sealed into 1/4" Pyrex tubing as H_2O , along with a measured quantity of zinc. Each sample tube is labeled and reacted in a heating block at 500°C for 35 minutes to generate hydrogen gas. Once the sample has been reacted, it is introduced into the sample side of the MS inlet system and analyzed against the working standard. Each analysis is given a unique label, using the lab number as the primary reference. Once the sample has been introduced into the MS, the analysis is computer controlled. The raw result is calculated by the manufacturer's software and recorded into a bound lab notebook, as well as being stored on computer hard disk and computer generated printout of results.

Maintenance The source region of the MS is periodically disassembled and cleaned. The filament is replaced as needed. Oil levels in mechanical vacuum pumps are checked frequently and maintained at the proper level. Turbomolecular pumps are lubricated according to the manufacturer's recommendations.

Calibration/Standardization The first run each day is a zero-enrichment where the standard is run against itself to check machine stability. Stable hydrogen isotope compositions are always reported as the difference between the ratios of the two isotopes of interest in the sample and the ratio in a primary reference standard. That is,

$$\delta D_{(\text{sample})} = \left[\left(\frac{{}^2\text{H}}{{}^1\text{H}}_{\text{sample}} - \frac{{}^2\text{H}}{{}^1\text{H}}_{\text{standard}} \right) / \frac{{}^2\text{H}}{{}^1\text{H}}_{\text{standard}} \right] \times 1000$$

The δ value is expressed in terms of per mil (‰), or parts per thousand.

In practice, the difference between the sample and an internal reference standard is measured and then the value relative to the primary standard is calculated by the instrument manufacturer's software. Two internal reference standards are used at Isotech which have been calibrated relative to several water standards available from the International Atomic Energy Agency and the National Institute of Standards and Technology. Standardization of the mass spectrometer involves analyzing one the reference standards against the other. This standardization is carried out at least once each day that analyses are to be conducted. In the rare event that the value obtained differs by more than 2 standard deviations from the expected value, the standardization is repeated with new aliquots of the reference standards. If the difference persists, the calibration of the reference gases is checked by having them analyzed by another laboratory, or by recalibrating them relative to NIST or IAEA standards. Aliquots of the NIST and IAEA standards are also periodically analyzed as samples as a further check on the calibration of the reference standard.

Replication Because of replicate preparation of samples, at least 10% of all analyses are replicates.

Reference Samples Because 10% of all samples prepared for stable isotope analysis are check samples or reference samples which have been previously analyzed, these samples also serve as check samples for the mass spectrometer.

Calculation All calculations are performed by the manufacturer's computer software. The raw data is then converted to final data using a spreadsheet on a personal computer. The spreadsheets are stored on computer hard disk and a copy is attached to the raw printouts for each batch of analyses.

IV. Gas Chromatographic Analysis of Gases

A. Analysis of hydrocarbons

Equipment Carle AGC 400 Gas Chromatograph which was custom designed by the manufacturer for Isotech. The GC is equipped with both thermal conductivity (TCD) and flame ionization (FID) detectors. Data processing is provided by a Nelson Analytical PC Interface coupled with a personal computer.

Method/Procedure At the start of each day, the detectors are turned on and the flow rate of the carrier gas is adjusted to an optimum level. The system is given 30 minutes for the thermistor detector to stabilize before the first sample is analyzed.

All gas sampling cylinders are fitted with a regulator containing a septum on the outlet. Before opening the valve on the cylinder, the air from the regulator is evacuated through a needle port connected to the inlet vacuum. If there is sufficient sample pressure, the outlet pressure is adjusted to approximately 50 psig.

The sample loop on the GC is evacuated to less than 60 microns between each sample. Samples are taken from the cylinder using a gas-lock syringe and injected through a septum into the evacuated sample loop. Air contamination from the syringe needle is evacuated while the loop is still open to the vacuum line. A large enough syringe is used to pressurize the sample loop with gas, and then the loop is adjusted to atmospheric pressure through a tube that is vented under water (to prevent air from leaking back into the vent). Sample identification is entered into the Nelson software and the method is downloaded into the PC interface. The run is then started by pressing a "run" keypad on the GC.

The Carle AGC 400 operates under isothermal conditions, utilizing several different packed columns and valve switching to separate the various components. Instrument configuration was designed by Carle specifically to meet the requirements of Isotech. Helium is used as the carrier gas. All valve switching during the analysis is computer-controlled. The detectors are connected to the PC interface, which converts the analog signal to digital and sends the data to the PC software for processing. The software for the Nelson system does component detection and area integration. The resulting component peak areas are then quantified by the software (given raw percent values) by comparing them to previously run standards. The lab technician checks the raw total for each analysis to ensure that all components have been detected. The raw total can vary from day to day depending on atmospheric pressure, with acceptable raw totals of 97% to 103%. The lab technician also checks all baselines for accuracy from the chromatograms shown on the computer screen. This raw computer record is maintained for each sample corresponding to its individual lab number. The raw percentage values for each sample are downloaded into the main sample database, and are normalized to 100% when the Analysis Report is generated.

Maintenance GC columns are periodically baked out according to manufacturer's instructions. Septa in the sampling valves are replaced as needed.

Calibration/Standardization Approximately 10 different reference standards are used for standardization of the Carle AGC 400 gas chromatograph. These standards were all purchased from Scott Specialty Gases. Most of these standards also contain some of the fixed gases. Normally all 10 are analyzed on the same day during a new standardization to minimize the effects of barometric pressure variations. The concentration for the individual components range from 15ppm to 99% (for methane). Maximum concentrations of other hydrocarbons are 12.6% for ethane, 7% for propane, 3% for butanes, and 1% for pentanes. These concentration ranges cover the majority of natural gases submitted for analysis. For each new standardization, the peak area of each concentration for each compound is inserted into a table within the Nelson software. This table is then accessed by the software, which uses point-to-point interpolation, to determine component concentrations for gas samples during analysis. At least four points are used for each component.

Reference Samples The reference sample used as the 1st run of each day and every tenth sample thereafter is representative of the majority of natural gas samples received for analysis. Reference samples are either created from a single sample or are mixed from several samples to give the desired composition. New reference samples are created before the current sample is depleted, and older reference samples are stored for future analysis and cross checks should problems arise. Data obtained for reference samples and expected results based on previous analyses can be provided as part of a QA/QC report.

Replication Every tenth analysis is a replicate. This replicate analysis is done approximately five samples following the check sample, thus a system check is performed at least every five analyses.

Calculation Each individual component for each sample is manually compared to the computer generated output to insure that the peak was labeled correctly and integrated correctly by the Nelson software.

B. Analysis of fixed gases

Equipment Carle AGC 400 Gas Chromatograph, Carle AGC 100 Gas Chromatograph with dual TCD detectors, and Nelson Analytical GC Interface.

Method/Procedure The procedure for analysis of fixed gases is identical to that for analysis of hydrocarbons, with two exceptions. First, for separation of oxygen and argon, an external column on the AGC 100 is used. This column operates at -78°C , therefore a dewar of dry ice/isopropyl alcohol is placed on the column before each run. At the end of each run, the dewar is removed and the column is warmed to room temperature to allow any other components held on the column to be passed. The column is flushed for 15 minutes between runs while the other

GC is in operation. The second difference is that the Carle AGC 100 is not computer controlled. This means that the technician must control the two valves manually. Both valves are switched to forward flow at the start of each analysis, and the Nelson PC interface is then started. Both valves are switched to backflush at predetermined times. The exact time of the switch is determined by monitoring the “real time” display on the computer screen. The lab technician checks all baselines to verify peak integration.

Maintenance GC columns are periodically baked out according to manufacturer's instructions. The septum on the injection valve is periodically replaced.

Calibration/Standardization Approximately 10 different reference standards are used to standardize the Carle AGC 100 and Carle AGC 400 for compositional analysis of fixed gases. All of these gases were purchased from Scott Specialty Gases. Some of these standards also contain hydrocarbons and are used for standardization of those compounds as well. Normally, all gases are analyzed on the same day during a new standardization to minimize the effects of barometric pressure. The concentration ranges of the standards cover the majority of natural gases submitted for analysis. For each new standardization, the peak area of each concentration for each compound is inserted into a table within the Nelson software. This table is then accessed by the software which uses point-to-point interpolation to determine component concentrations for gas samples during analysis.

Check Sample The reference sample used as the 1st run of each day and every tenth sample thereafter is chosen based on its composition. All reference samples contain at least nitrogen and carbon dioxide, and most also contain hydrogen, helium, and argon. The reference samples are either a single sample meeting the above requirements, or are mixtures of several samples to give the desired composition. New reference samples are created before the current sample is depleted, and older reference samples are stored for future analysis and cross checks should problems arise. Data obtained for reference samples and expected results based on previous analyses can be provided as part of a QA/QC report.

Replication Every tenth analysis is a duplicate. This duplicate analysis is performed approximately five samples following the check sample, thus a system check is performed at least every five analyses.

Calculation Each individual component for each sample is manually compared to the computer generated output to insure that the peak was labeled correctly and integrated correctly by the Nelson software.

V. Radiocarbon Analysis of Prepared Samples

Radiocarbon analyses of purified CO₂ samples prepared by Isotech are currently being subcontracted to either Beta Analytic Inc., Coral Gables, Florida or to Illinois State Geological Survey, Champaign, Illinois. Beta Analytic is the largest commercial radiocarbon dating laboratory in the world. The attached QA/QC plans have been provided by

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